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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : C07D 311/16, C07C 69/618, G02F 1/1337 | A1

(11) International Publication Number: **WO 00/55151**

(43) International Publication Date: 21 September 2000 (21.09.00)

(21) International Application Number: PCT/GB00/00825

(22) International Filing Date: 7 March 2000 (07.03.00)

(30) Priority Data:
9905579.0 12 March 1999 (12.03.99) GB

(71) Applicant *(for all designated States except US)*: THE SECRETARY OF STATE FOR DEFENCE [GB/GB]; Defence Evaluation & Research Agency, Ively Road, Farnborough, Hampshire GU14 0LX (GB).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: OWEN, Gareth, James [GB/GB]; Department of Chemistry, University of Hull, Hull, Humberside HU6 7RX (GB). JACKSON, Peregrin, Orr [GB/GB]; Department of Chemistry, University of Hull, Hull, Humberside HU6 7RX (GB). O'NEIL, Mary [GB/GB]; Department of Chemistry, University of Hull, Hull, Humberside HU6 7RX (GB). KELLY, Stephen, Malcolm [GB/GB]; Department of Chemistry, University of Hull, Hull, Humberside HU6 7RX (GB).

(74) Agent: BOWDERY A., O.; The Secretary of State for Defence, DERA Intellectual Property Department, A4 Building Rm G016, Ively Road, Farnborough, Hampshire GU14 0LX (GB).

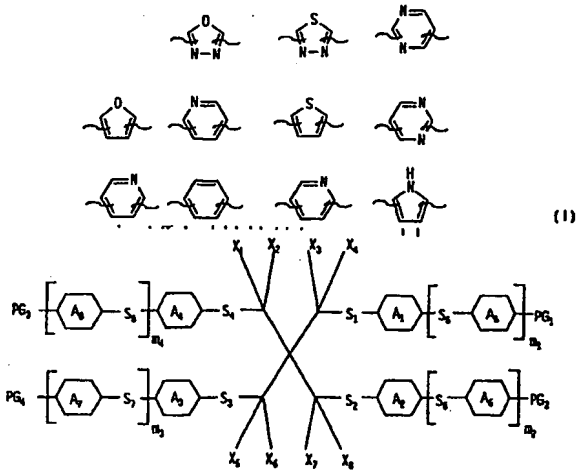
(81) Designated States: GB, JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: PHOTOACTIVE PENTAERYTHRITOL DERIVATIVES AND ORIENTATION LAYERS

(57) Abstract

Compounds of formula (I) may be used as alignment layers in liquid crystal devices wherein: X_{1-8} are each independently selected from: H, halogen, CN, OH, straight or branched chain alkyl having from 1 to 16 carbon atoms, where one or more non-adjacent CH_2 groups may be substituted by CH(CN), $CH(CF_3)$, CHF, CHCl, $CH(CH_3)$;S_{1-8} are spacer units; PG_{1-4} are photopolymerisable/dimerisable groups; m_1, m_2, m_3, and m_4 are each independently selected from the integers 1 and 0; A_{1-8} are each independently selected from the aromatic rings where: ~ indicates a sigma bond between part of the molecule shown in formula (I) and a carbon atom at any position in one of the aromatic rings; and where the CH groups present in the aromatic rings may each be independently substituted by C(CN), $C(CF_3)$, C–halogen, $C(CH_3)$, CR, where R is selected from hydrogen, straight or branched chain alkyl and may include from 1 to 8 carbon atoms and including where one or more non-adjacent CH_2 groups may be substituted by CH(CN), $CH(CF_3)$, CHF, CHCl, $CH(CH_3)$.



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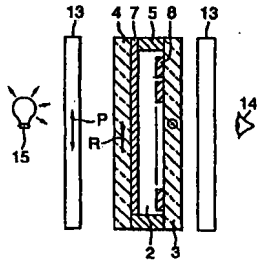

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Photoactive Pentaerythritol Derivatives and Orientation Layers

The present invention describes materials and methods for achieving alignment of liquid crystal materials on a substrate surface and devices fabricated using these methods and materials.

Liquid crystal display devices (LCDs) or light shutters generally comprise a layer of liquid crystalline material between two solid substrates to form a cell. These substrates are generally coated with a conducting material, such as Indium/Tin Oxide (ITO) to form electrodes or electrode patterns. An electric field applied across the cell or between the electrodes switches the liquid crystal between different molecular arrangements or states. Thus the light transmission through the cell can be modulated depending on the cell configuration, the type of liquid crystalline material, the presence of polarisers, etc. A preferred molecular alignment direction and pretilt angle (θ) is imparted by an alignment layer on top of the electrodes and in contact with the liquid crystalline material.

It is well known in the art that fabrication of liquid crystal devices which have advantageous performance and low defect densities requires control of the alignment of the liquid crystalline material at the surfaces of the device. Different types of liquid crystal alignment have been described. Homeotropic alignment refers to an alignment in which the unique optical axis of a liquid crystal phase is held perpendicular to the adjacent surface.

Planar alignment, sometimes referred to as homogeneous alignment, refers to alignment in which the unique optic axis of the liquid crystal phase lies parallel to the adjacent surface. Planar alignment may also impose a direction in which the optic axis of the liquid crystal lies in the plane of the adjacent surface.

Tilted planar alignment or tilted homogeneous alignment refer to alignment in which the liquid crystal unique optic axis lies at an angle, termed the pretilt angle (θ) from the plane of the adjacent surface. The pretilt angle may be as small as a fraction of one degree or as large as several tens of degrees.

Tilted homeotropic alignment refers to an alignment in which the optic axis of the liquid crystal lies tilted away from the normal to the adjacent surface. This deviation is again termed a pretilt angle.

In liquid crystal devices, said alignment geometries are chosen and used in combination to achieve specific optical and electro-optic properties from the device and may be combined in new ways or with new liquid crystalline mixtures to provide new types of devices.

Several methods are known in the art by which defined liquid crystal alignment may be achieved. Deposition of a polymer layer, for example a polyimide layer, on the substrate surface followed by mechanical rubbing provides a pretilted planar alignment. A planar alignment or tilted planar alignment may also be achieved by evaporating a variety of inorganic substances, for example SiO_x, onto the surface from an oblique angle of incidence. A disadvantage of this method is that it requires slow and costly vacuum processing. A further disadvantage is that the resulting evaporated layer may show a high capacity to absorb contaminants onto itself from the environment or from other materials used in fabrication of the device.

A homeotropic alignment can be obtained by depositing a surfactant, for example a quaternary ammonium salt, onto the surface from solution in a suitable solvent. A disadvantage of this treatment is that the resistivity of the liquid crystal device may be lowered by the surfactant and the resulting alignment may also show poor stability.

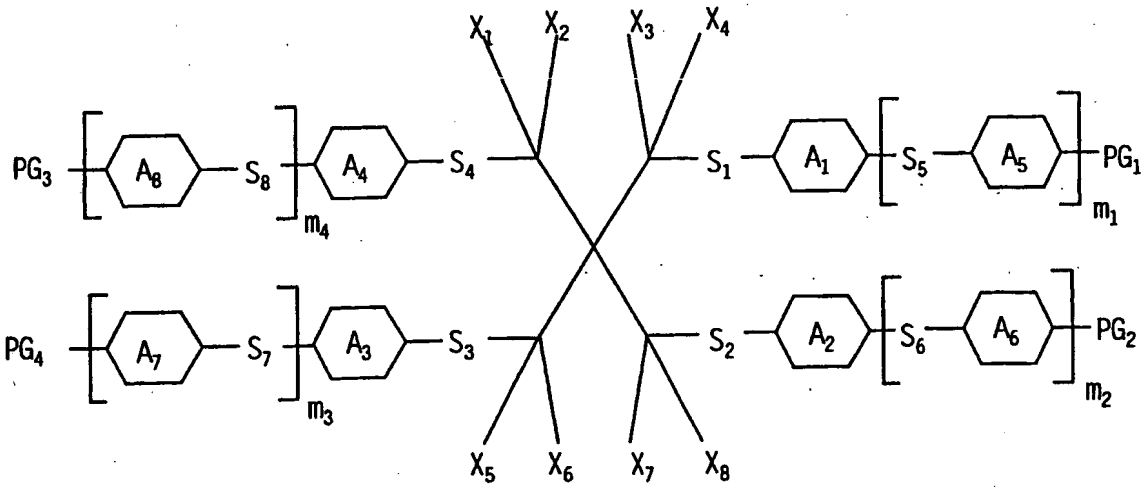
Structured alignment patterns of subpixel size and above can be achieved by illumination of a polymer layer containing photochemically orientable dyes or photochemically dimerisable and/or isomerisable molecules, as described, for example, in EP-A-0445629. A disadvantage of this method is that the solubility of the dye molecules in the polymer matrix is limited and the chemical and photochemical stability over time is insufficient.

Another method for achieving structured non-contact orientation is the photodimerisation of polymers incorporating photodimerisable groups, such as cinnamate or coumarin derivatives, as described, for example, in Jpn. J. Appl. Phys., Vol., 31, 2155 (1995) and EP-A-9410699.0. A disadvantage of these materials is the polydispersity of the materials produced by polymerisation. This requires, for example, different solution concentrations for spin coating depending on the average molecular weights of the polymers which can not be determined with any great accuracy and which are often not reproducible from one batch to another. This can give rise to unreproducible alignment as well as also requiring repeated purification cycles of the polymer product in order to remove unreacted monomer and oligomers. The attachment of low molar mass photoreactive units to monodispersed polymer backbones can lead to

polymers with unreacted sites, which can give rise to dielectric breakdown of cells containing such materials. This is especially important for active matrix devices.

An object of this invention is to provide means of achieving a defined surface alignment of a liquid crystalline material on a substrate surface, which does not require mechanical rubbing or other methods of physical contact which may damage the surface or structures on the surface. This is especially important for active matrix displays based on the use of surface mounted thin film transistors. Static electricity or dust caused by mechanical rubbing or buffing polymer layers, such as polyimide or polyamide, in order to induce a unidirectional alignment due to microgrooves can cause defects in thin film transistors and lead to dielectric breakdown. Such alignment layers also suffer from the disadvantage that the microgrooves possess inherent defects themselves, which can result in random phase distortion and light scattering. This impacts detrimentally on the optical appearance of the displays or the efficiency of the light shutters. Additionally, mechanical buffing does not allow locally oriented regions of the surface to be aligned with different azimuthal angles. This is a substantial drawback since sub-pixelisation can lead to higher contrast and an improved optical efficiency.

According to this invention materials are provided of Formula I:



Formula I

where

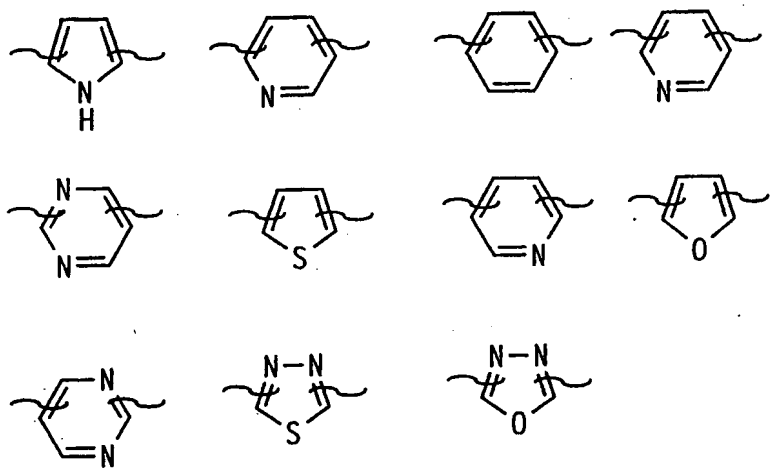
X_{1-8} are each independently selected from: H, halogen, CN, OH, straight or branched chain alkyl having from 1 to 16 carbon atoms, where one or more non-adjacent CH_2 groups may be substituted by CH(CN), $CH(CF_3)$, CHF, CHCl, $CH(CH_3)$;

S_{1-8} are spacer units;

PG_{1-4} are photopolymerisable/dimerisable groups

m_1, m_2, m_3, and m_4 are each independently selected from the integers 1 and 0;

A_{1-8} are each independently selected from the aromatic rings:



where ~ indicates a sigma bond between part of the molecule shown in formula I and a carbon atom at any position in one of the aromatic rings;

and where the CH groups present in the aromatic rings may each be independently substituted by C(CN), $C(CF_3)$, C-halogen, $C(CH_3)$, CR, where R is selected from straight or branched chain alkyl and may include from 1 to 8 carbon atoms and including where one or more non-adjacent CH_2 groups may be substituted by CH(CN), $CH(CF_3)$, CHF, CHCl, $CH(CH_3)$.

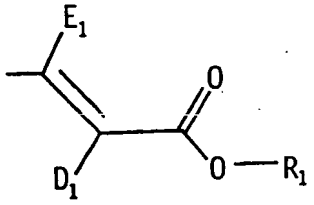
Preferably the spacer groups S_{1-4} are, independently of one another, selected from groups having the general formula:

$$L_1—(CH_2)_n—L_2$$

where: n = 1 to 30, where each CH_2 group present in the chain linking L_1 and L_2 may be independently substituted by CH(CN), $CH(CF_3)$, CHF, CHCl, $CH(CH_3)$, L_1 and L_2 are independently selected from: single covalent bond, O, COO, OOC, CH_2O, and OCH_2. More preferably S_{1-4} are independently selected from oxycarbonylalkanoyloxy, oxyalkoxy, oxycarbonylalkoxy, oxyalkanoyloxy, oxycarbonylphenoxyalkanoyloxy, oxyalkoxyalkyl containing from 1-16 carbon atoms.

In a preferred embodiment spacer groups S_{5-8} are each independently selected from: COO, OOC, C≡C, C=C, single covalent bond.

Preferably the photopolymerisable/dimerisable groups PG_{1-4} are each independently selected from:



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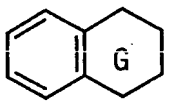
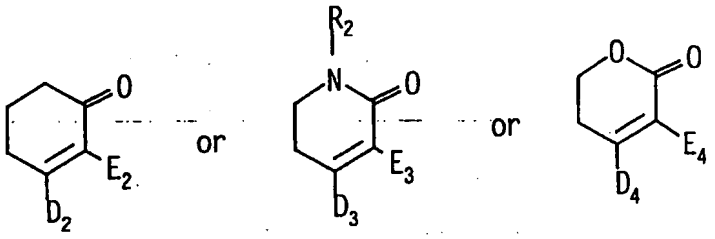


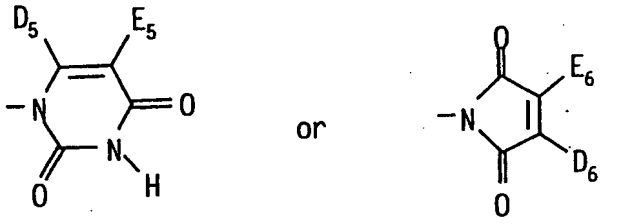
or

where a sigma bond exists between part of the molecule shown in formula I and any one of the four C atoms that are in the benzene ring to which G is fused and that do not form part of the ring G; and where CH groups present in the benzene ring to which the ring G is fused may each be independently substituted by C(CN), $C(CF_3)$, C-halogen, $C(CH_3)$, CR, where R is selected from straight or branched chain alkyl and may include from 1 to 8 carbon atoms and including where one or more non-adjacent CH_2 groups may be substituted by CH(CN), $CH(CF_3)$, CHF, CHCl, $CH(CH_3)$;

where G is independently selected from:



and where J is independently selected from:



R_1 may be H, halogen, CN, NO_2, NCS, SCN, alkyl with 1 to 12 carbon atoms which is optionally substituted with one or more fluorines and in which optionally 1 or 2 non-adjacent methylene units (CH_2) can be replaced by oxygen, COO, OOC, CO and/or CH=CH;

R_2 may be H or C_{1-10} alkyl;

D_1 may be H, alkyl or alkoxy with 1 to 8 carbon atoms, trifluoromethyl, or phenyl which may be substituted from one and up to and including all available substitution positions with one or more of the groups selected from CN, halogen, NO_2;

E_1 may be H, alkyl or alkoxy with 1 to 8 carbon atoms, cyano, or $COOR_5$;

R_5 may be C_{1-10} alkyl.

D_2 may be H, alkyl or alkoxy with 1 to 8 carbon atoms, trifluoromethyl, or phenyl which may be substituted from one and up to and including all available substitution positions with one or more of the groups selected from CN, halogen, NO_2;

E_2 may be H, alkyl or alkoxy with 1 to 8 carbon atoms, cyano, or $COOR_6$;
R_6 may be C_{1-10} alkyl.

D_3 may be H, alkyl or alkoxy with 1 to 8 carbon atoms, trifluoromethyl, or phenyl which may be substituted from one and up to and including all available substitution positions with one or more of the groups selected from CN, halogen, NO_2;
E_3 may be H, alkyl or alkoxy with 1 to 8 carbon atoms, cyano, or $COOR_7$;
R_7 may be C_{1-10} alkyl.

D_4 may be H, alkyl or alkoxy with 1 to 8 carbon atoms, trifluoromethyl, or phenyl which may be substituted from one and up to and including all available substitution positions with one or more of the groups selected from CN, halogen, NO_2;
E_4 may be H, alkyl or alkoxy with 1 to 8 carbon atoms, cyano, or $COOR_8$;
R_8 may be C_{1-10} alkyl.

D_5 may be H, alkyl or alkoxy with 1 to 8 carbon atoms, trifluoromethyl, or phenyl which may be substituted from one and up to and including all available substitution positions with one or more of the groups selected from CN, halogen, NO_2;
E_5 may be H, alkyl or alkoxy with 1 to 8 carbon atoms, cyano, or $COOR_9$;
R_9 may be C_{1-10} alkyl.

D_6 may be H, alkyl or alkoxy with 1 to 8 carbon atoms, trifluoromethyl, or phenyl which may be substituted from one and up to and including all available substitution positions with one or more of the groups selected from CN, halogen, NO_2;
E_6 may be H, alkyl or alkoxy with 1 to 8 carbon atoms, cyano, or $COOR_{10}$;
R_{10} may be C_{1-10} alkyl.

Examples of the term "alkyl with 1 to 12 carbon atoms which is optionally substituted with one or more fluorines and in which optionally 1 or 2 non-adjacent methylene units (CH_2) can be replaced by oxygen, COO, OOC, CO and/or CH=CH" include in the present application straight-chain and branched (optionally chiral) residues such as alkyl, alkenyl, alkoxy, alkenyloxy, alkoxyalkyl, alkoxyalkenyl, 1-fluoroalkyl, terminal trifluoromethylalkyl, terminal difluoromethylalkyl, terminal trifluoromethylalkoxy, and the like with 1 or, 2 to 16 carbon atoms. Examples of preferred residues are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, 1-

methylpropyl, 1-methylheptyl, 2-methylbutyl, 3-methyl pentyl, vinyl, 1E-propenyl, 1E-butenyl, 1E-pentenyl, 3-butenyl, 3E-pentenyl, 3E-hexenyl, 3E-hexenyl, 4-pentenyl, 4Z-hexenyl, 5-hexenyl, 6-heptenyl, 7-octenyl, methoxy, ethoxy, propyloxy, butyloxy, pentyloxy, hexyloxy, octyloxy, 1-methylpropyloxy, 1-methylheptyloxy, 2-methylbutyloxy, 1-fluoropropyl, 2-fluoropropyl, 2,2-difluoropropyl, 3-fluoropropyl, 3,3-difluoropropyl, 3,3,3-trifluoropropyl and the like. Especially preferred residues possess 1 or, respectively, 2 to 6 carbon atoms.

The term "halogen" may represent in the present application fluorine, chlorine, bromine and iodine, but especially fluorine and chlorine.

According to an aspect of this invention a method is provided for forming an alignment layer on a surface of a liquid crystal cell wall, the method comprising the steps: depositing a layer of a material comprising at least one compound of Formula I on the surface; and exposing the material to actinic radiation.

Preferably the method for forming an alignment layer further comprises the step of controlling the exposure time and/or intensity of the actinic radiation used to provide a selected value of pretilt in a liquid crystal placed in contact with the exposed layer.

Preferably the radiation includes light, with a wavelength of 250-450nm. More preferably the radiation is light with a wavelength of 300-400nm.

According to a further aspect of this invention a liquid crystal device comprises a layer of a liquid crystal material contained between two cell walls both carrying electrode structures and surface treated to provide an alignment layer for liquid crystal molecules;

characterised in that:

the alignment layer comprises a compound of Formula 1 that has been exposed to actinic radiation.

Preferably the alignment layer comprises a compound of Formula I that has been exposed to actinic radiation, the exposure time and/or intensity of the actinic radiation used being

controlled to provide a selected value of pretilt in a liquid crystal placed in contact with the exposed layer.

Preferably the radiation includes light, with a wavelength of 250-450nm. More preferably the radiation is light with a wavelength of 300-400nm.

Compounds of Formula I can be prepared by various routes from commercially available starting materials. Typically tetrakis(hydroxymethyl)methane (pentaerythritol) can be esterified with ω-halogenoalkanoic acids in the presence of N,N-dicyclohexylcarbodiimide and 4-(dimethylamino)pyridine and a polar solvent, such as N,N-dimethylformamide or dichloromethane. The resultant bromides can then be alkylated in a Williams ether synthesis with phenols incorporating a photoisomerisable/dimerisable group, such as coumarin or cinnamate, in the presence of a base, such as potassium carbonate, and a polar solvent, such as cyclohexanone or ethyl-methylketone. The bromides can also be esterified with a photoisomerisable/dimerisable group, such as cinnamic acids, in the presence of DBU and a non polar solvent, such as toluene or benzene. Similarly pentaerythritol can be alkylated with ω-halogenoalkanols protected, for example as the THP derivative, in the presence of base, such as potassium tert.-butylate, and a polar solvent, such as 1,2-dimethoxyethane or ethylene glycol dimethyl ether. After deprotection the resultant alcohols can then be esterified with a photoisomerisable/dimerisable group, such as aromatic acids incorporating a cinnamate or coumarin moiety, in the presence of N,N-dicyclohexylcarbodiimide and 4-(dimethylamino)pyridine and a polar solvent, such as N,N-dimethylformamide or dichloromethane. The alcohols can also be alkylated in a Mitsunobu reaction, with a photoisomerisable/dimerisable group, such as 6-hydroxycoumarin, 7-hydroxycoumarin (umbelliferone) or alkyl hydroxycinnamates, in the presence of a dehydrating agent, such as diethyl azodicarboxylate and triphenyl phosphine, and a polar solvent, such as tetrahydrofuran or N,N-dimethylformamide.

The photocross-linkable groups, such as cinnamic acids, cinnamate esters, cinnamonitriles, styrenes, stilbenes, vinylnaphthalenes, vinylpyridines, maleimides, thymines, coumarins, are generally are either commercially available or readily accessible, for example coumarin and cinnamate derivatives can be prepared according to literature methods, such as the Perkin, Pechmann, Knoevenagel, Wittig-Horner, Heck or sigmatropic rearrangement reactions (Organic Reactions, **1**, 210, 1942; Organic Reactions, **15**, 204, 1967; Synthesis, 131, 1978; J. Mol. Cat., 88, L113, 1994; J. Chem. Soc. Perkin Trans. I, 1753, 1987).

In order to obtain alignment layers in regions selectively limited by area, a solution of the photoactive pentraerythritol derivative can, for example, firstly be prepared and then spread out using a spin-coating apparatus on a carrier coated with an electrode , e.g., a glass plate coated with indium-tin oxide (ITO) such that homogeneous layers of 0.05-50 µm thickness result. Subsequently or simultaneously, irradiation can be applied to the region to be isomerised and/or dimerised (cross-linked), e.g., with a mercury high pressure lamp, a xenon lamp or a UV laser utilising a polariser and optionally a mask for the formation of structures. The duration and irradiation depends on the capacity of the individual lamps and can vary from a few minutes to several hours. The cross-linking can, however, also effected by irradiating the homogeneous layer using filters which, e.g., let through only radiation suitable for the cross-linking reaction. Photosensitisors, such as acetophenone or benzophenone may be added to shorten the illumination time required for cross-linking. Non-zero tilt angles (θ) may be induced by illumination with plane polarised light from a non-perpendicular angle to the plane of the substrate.

The invention will now be described, by way of example only, with reference to the following examples and diagrams:

Figure 1 is a plan view of a matrix multiplex addressed liquid crystal display;
Figure 2 is a cross-section of a display such as Figure 1 used in a transmissive mode;
Figure 3 is similar to Figure 2 but operates in a reflective mode; and
Figure 4 is a schematic representation of the apparatus used to illuminate the photocross-linkable propane derivatives on a suitable substrate to be used as part of a liquid crystal device.

The device of Figures 1, 2 and 3 comprises a liquid crystal cell 1 formed by a layer of a liquid crystal material 2 contained between two glass walls 3, 4 spaced typically 1 to 15µm apart by a spacer ring 5. The inside faces of both walls 3, 4 are coated with electrodes 6. The electrodes may be of sheet like form covering the complete wall, or formed into for example, strip electrodes to provide an array of addressable electrode intersections. The walls are also coated with an aligning layer (not shown) of material described by the current invention.

If the material 2 is nematic then the device may be the known super twisted nematic device, also known as a STN device. In this case polarisers 13 are used to distinguish between the device voltage ON and OFF states.

The liquid crystal material may be nematic, chiral nematic (cholesteric), or smectic (e.g., ferroelectric) material. The device may be used as a display device, e.g., displaying alpha numeric information, or an x, y matrix displaying information. alternatively the device may operate as a shutter to modulate light transmission, e.g., as a spatial light modulator, or as a privacy window.

For passive matrix devices (shown in figure 1) strip like row electrodes 6_1 to 6_m, e.g. of $InSnO_2$ are formed on one wall 3 and similar column electrodes 7_1 to 7_n formed on the other wall 4. With m-row electrodes and n-column electrodes this forms an mxn matrix of addressable elements. Each element is formed by the interaction of a row and column electrode. For active matrix devices a discrete nonlinear device eg a transistor or diode is associated with each pixel.

For the passive matrix device a row driver supplies voltage to each row electrode 6. Similarly a column drive 9 supplies voltages to each column electrode 7. Control of applied voltages is from a control logic 10 which receives power from a voltage source 11 and timing from a clock 12.

For an active device e.g., a thin film transistor active matrix liquid crystal device (TFT AMLCD) three types of electrodes are present, pixel, scanning and signal electrodes as well as a common electrode on the opposite side of the liquid crystal. The control electrode operates the gate such that the voltage on the signal electrode is applied to the relevant pixel electrode.

An example of the use of a material and device embodying the present invention will now be described with reference to Figure 2.

The liquid crystal device consists of two transparent plates, 3 and 4, for example made from glass, in the case of an active matrix device these will usually be ofaluminosilicate (alkali free) glass often with a passivation layer of SiO_2. For an active matrix display the active devices eg thin film transistors, are fabricated and the colour filter layer is added for a full colour display. These plates are coated on their internal face with transparent conducting electrodes 6 and 7,

often ITO which is patterned using photolithography techniques. The transparent plates 3 and 4 are coated with a photoactive sample, comprising one or more compounds according to the invention. A typical coating procedure involves the dissolution of one of the compounds of the invention in a solvent, for example cyclopentanone, followed by spin coating of the photoactive compound on the transparent plate. Once the photoactive compound has been coated onto the plates it is exposed to actinic radiation to induce cross-linking of the photoactive molecules. The cross-linking process can be monitored by measuring the birefringence of the alignment layer. The intersections between each column and row electrode form an x, y matrix of addressable elements or pixels. A spacer 5 e.g. of polymethyl methacrylate separates the glass plates 3 and 4 to a suitable distance e.g. 2-7 microns preferably 4-6 microns. Liquid crystal material 2 is introduced between glass plates 3,4 by filling the space in between them. This may be done by flow filling the cell using standard techniques. The spacer 5 is sealed with an adhesive in a vacuum using an existing technique. Polarisers 13 may be arranged in front of and behind the cell.

The device may operate in a transmissive or reflective mode. In the former, light passing through the device, e.g. from a tungsten bulb, is selectively transmitted or blocked to form the desired display. In the reflective mode a mirror, or diffuse reflector, (16) is placed behind the second polariser 13 to reflect ambient light back through the cell and two polarisers. By making the mirror partly reflecting the device may be operated both in a transmissive and reflective mode.

The alignment layers have two functions, one to align contacting liquid crystal molecules in a preferred direction and the other to give a tilt to these molecules - a so called surface tilt - of a few degrees typically around 4° or 5°. In an alternative embodiment a single polariser and dye material may be combined. The materials of the current invention may also be used in LCDs with an actively addressed matrix e.g. thin film transistors (TFT-LCDs) or a passively addressed matrix e.g., dual scan STN.

The apparatus of Figure 4 used to generate photoinduced anisotropy in a photoactive sample 17, comprising a photoactive pentaerythrol derivative according to the invention, using linearly polarised UV light comprises a radiation source e.g. an argon ion laser 18 (Spectra Physics, Model 2045). The laser beam operating at 300.5nm has a polarisation direction (E). The laser beam was expanded by using a quartz lens beam expander 19. The film anisotropy is measured by determining the induced birefringence against UV exposure time using a He-Ne laser 20 (632.8nm) modulated by a rotating chopper 21. The probing wavelength does not

perturb the anisotropy inducing process since it is far away from any intrinsic absorption band in either the starting material or photoproduct. During the UV exposure of the sample, the photoinduced birefringence was monitored using two crossed polarisers, P1 and P2 arranged at +/- 45° with respect to the vertical polarisation of the UV laser beam. The intensity of the beam from the probing He-Ne laser 20, which then passed through the sample, was detected by a photodetector 22. The birefringence measuring signal taken from the photodetector 22 was processed by a phase sensitive lock-in amplifier 20 and recorded by a computer 24. Data were plotted as birefringence versus UV exposure time. In this way the cross-linking process can be induced and monitored.

The photocross-linkable pentaerythritol derivatives and resultant alignment layers may be produced as described, by way of example only, in the following examples; K signifies the crystalline state, I signifies the isotropic phase, T_g is the glass transition temperature.

Example 1. Preparation of 1,2,3,4-tetrakiskis(8-[2-oxo-2H-1-benzopyran-7-yloxy]octanoyloxy)pentaerythritol.

A mixture of 3.0 g 1,2,3,4-tetrakis(8-bromooctanoyloxy)pentaerythritol, 2.0 g 7-hydroxycoumarin, 5.0 g anhydrous potassium carbonate and 50 ml ethyl-methyl ketone was heated under gentle reflux overnight. The reaction mixture was filtered to remove inorganic material and the filtrate evaporated down. The residue was purified by column chromatography on silica gel using hexane/ethyl acetate (1/1 v/v) as eluent and recrystallisation from acetonitrile to yield 2.1 g of 1,2,3,4-tetrakis(8-[2-oxo-2H-1-benzopyran-7-yloxy]octanoyloxy)pentaerythritol as an oil.

The 1,2,3,4-tetrakis(8-bromooctanoyloxy)pentaerythritol required as starting material was prepared as follows:

12.0 g Dicyclohexylcarbodiimide was added to a solution of 2.0 g pentaerythritol, 13.0 g 8-bromooctanoic acid, 1.8 g 4-(dimethylamino)pyridine and 50 ml dichloromethane at 0°C. The reaction mixture was stirred overnight at room temperature, filtered to remove inorganic material and the filtrate evaporated down. The residue was purified by column chromatography on silica gel using hexane/ethyl acetate (1/1 v/v) as eluent and recrystallisation from acetonitrile to yield 6.5 g of 1,2,3,4-tetrakis(8-bromooctanoyloxy)pentaerythritol as an oil.

The following compounds can be prepared in an analogous manner:

1,2,3,4-tetrakis(3-[2-oxo-2H-1-benzopyran-7-yloxy]propanoyloxy)pentaerythritol.
1,2,3,4-tetrakis(4-[2-oxo-2H-1-benzopyran-7-yloxy]butanoyloxy)pentaerythritol.
1,2,3,4-tetrakis(5-[2-oxo-2H-1-benzopyran-7-yloxy]pentanoyloxy)pentaerythritol.
1,2,3,4-tetrakis(6-[2-oxo-2H-1-benzopyran-7-yloxy]hexanoyloxy)pentaerythritol.
1,2,3,4-tetrakis(7-[2-oxo-2H-1-benzopyran-7-yloxy]heptanoyloxy)pentaerythritol.
1,2,3,4-tetrakis(9-[2-oxo-2H-1-benzopyran-7-yloxy]nonanoyloxy)pentaerythritol.
1,2,3,4-tetrakis(10-[2-oxo-2H-1-benzopyran-7-yloxy]decanoyloxy)pentaerythritol.
1,2,3,4-tetrakis(3-[2-oxo-2H-1-benzopyran-6-yloxy]propanoyloxy)pentaerythritol.
1,2,3,4-tetrakis(4-[2-oxo-2H-1-benzopyran-6-yloxy]butanoyloxy)pentaerythritol.
1,2,3,4-tetrakis(5-[2-oxo-2H-1-benzopyran-6-yloxy]pentanoyloxy)pentaerythritol.
1,2,3,4-tetrakis(6-[2-oxo-2H-1-benzopyran-6-yloxy]hexanoyloxy)pentaerythritol.
1,2,3,4-tetrakis(7-[2-oxo-2H-1-benzopyran-6-yloxy]heptanoyloxy)pentaerythritol.
1,2,3,4-tetrakis(8-[2-oxo-2H-1-benzopyran-6-yloxy]octanoyloxy)pentaerythritol.
1,2,3,4-tetrakis(9-[2-oxo-2H-1-benzopyran-6-yloxy]nonanoyloxy)pentaerythritol.
1,2,3,4-tetrakis(10-[2-oxo-2H-1-benzopyran-6-yloxy]decanoyloxy)pentaerythritol.
1,2,3,4-tetrakis[3-(4-[(*E*)-methoxycarbonylethenyl]phenoxy)propanoyloxy]pentaerythritol.
1,2,3,4-tetrakis[3-(4-[(*E*)-ethoxycarbonylethenyl]phenoxy)propanoyloxy]pentaerythritol.
1,2,3,4-tetrakis[4-(4-[(*E*)-ethoxycarbonylethenyl]phenoxy)butanoyloxy]pentaerythritol.
1,2,3,4-tetrakis[5-(4-[(*E*)-ethoxycarbonylethenyl]phenoxy)pentanoyloxy]pentaerythritol.
1,2,3,4-tetrakis[6-(4-[(*E*)-ethoxycarbonylethenyl]phenoxy)hexanoyloxy]pentaerythritol.
1,2,3,4-tetrakis[7-(4-[(*E*)-ethoxycarbonylethenyl]phenoxy)heptanoyloxy]pentaerythritol.
1,2,3,4-tetrakis[8-(4-[(*E*)-ethoxycarbonylethenyl]phenoxy)octanoyloxy]pentaerythritol.
1,2,3,4-tetrakis[8-(4-{2-[(*E*)-ethoxycarbonylethenyl]thiophen-5-yl}phenoxy)octanoyloxy]pentaerythritol.

1,2,3,4-tetrakis[8-(4-{2-[(*E*)-ethoxycarbonylethenyl]furan-5-yl}phenoxy)octanoyloxy]pentaerythritol.

1,2,3,4-tetrakis[8-(4-{2-[(*E*)-ethoxycarbonylethenyl]pridin-5-yl}phenoxy)octanoyloxy]pentaerythritol.

1,2,3,4-tetrakis[8-(4-{2-[(*E*)-ethoxycarbonylethenyl]primidin-5-yl}phenoxy)octanoyloxy]pentaerythritol.

1,2,3,4-tetrakis[3-(4-[(*E*)-ethoxycarbonylethenyl]biphenyl-4'-yloxy)propanoyloxy]pentaerythritol.

1,2,3,4-tetrakis[4-(4-[(*E*)-ethoxycarbonylethenyl]biphenyl-4'-yloxy)butanoyloxy]pentaerythritol.

1,2,3,4-tetrakis[5-(4-[(*E*)-ethoxycarbonylethenyl]biphenyl-4'-yloxy)pentanoyloxy]pentaerythritol.

1,2,3,4-tetrakis[6-(4-[(*E*)-ethoxycarbonylethenyl]biphenyl-4'-yloxy)hexanoyloxy]pentaerythritol, Mpt 187 °C.

1,2,3,4-tetrakis[7-(4-[(*E*)-ethoxycarbonylethenyl]biphenyl-4'-yloxy)heptanoyloxy]pentaerythritol.

1,2,3,4-tetrakis[8-(4-[(*E*)-ethoxycarbonylethenyl]biphenyl-4'-yloxy)octanoyloxy]pentaerythritol.

Example 2. Preparation of 1,2,3,4-tetrakis(4-[(*E*)-ethoxycarboxyethenyl]biphenyl-4'-yloxy)pentaerythritol.

2.6 g Diethyl azodicarboxylate was added to a solution of 3.7 g 4-[(*E*)-ethoxycarboxyethenyl]-4'-hydroxybiphenyl, 0.57 g pentaerythritol, 3.9 g triphenyl phosphine and 50 ml tetrahydrofuran at 0°C. The reaction mixture was stirred overnight at room temperature and then evaporated down with silica gel. The resultant powder was purified by column chromatography on silica gel using hexane/ethyl acetate (1/1 v/v) as eluent and recrystallisation from ethanol to yield 2.1 g of 1,2,3,4-tetrakis(4-[(*E*)-ethoxycarboxyethenyl]biphenyl-4'-yloxy)pentaerythritol; Mpt 241 °C.

The 4-[(*E*)-ethoxycarboxyethenyl]-4'-hydroxybiphenyl required as starting material is prepared as follows:

A mixture of 10.0 g 4-bromo-4'-hydroxybiphenyl, 6.9 g methyl acrylate, 8.1 g triethylamine, 0.1 g palladium(II)acetate, 0.4 g tri(o-toluyl)phosphine and 30 ml acetonitrile was heated under gentle reflux overnight. The reaction mixture was diluted with 200 ml acetonitrile, filtered to remove inorganic material and the filtrate evaporated down. The residue was purified by precipitation from a dichloromethane solution into hexane and recrystallisation from acetonitrile to yield 7.2 g of 4-[(*E*)-ethoxycarboxyethenyl]-4'-hydroxybiphenyl; Mpt 228 °C.

The following compounds can be prepared in an analogous manner:

1,2,3,4-tetrakis(2-oxo-2H-1-benzopyran-7-yloxy)pentaerythritol.
carbonyl)phenoxy]dodecanoyloxy)propane.
1,2,3,4-tetrakis(2-oxo-2H-1-benzopyran-6-yloxy)pentaerythritol.
carbonyl)phenoxy]dodecanoyloxy)propane.
1,2,3,4-tetrakis(4-[(*E*)-methoxycarboxyethenyl]phenoxy)pentaerythritol.
1,2,3,4-tetrakis(4-[(*E*)-ethoxycarboxyethenyl]phenoxy)pentaerythritol.
1,2,3,4-tetrakis(4-[(*E*)-methoxycarboxyethenyl]biphenyl-4'- yloxy)pentaerythritol.
1,2,3,4-tetrakis(4-[(*E*)-methoxycarboxyethenyl]-p-terphenyl-4"- yloxy)pentaerythritol.

Example 3. Preparation of 1,2,3,4-tetrakiskis(6-[4-{2-oxo-2H-1-benzopyran-7-yloxycarbonyl}phenoxy]hexanoyloxy)pentaerythritol.

A mixture of 0.7 g 1,2,3,4-tetrakis(5-bromohexanoyloxy)pentaerythritol, 1.0 g 2-oxo-2H-1-benzopyran-7-yl 4-hydroxybenzoate, 5.0 g anhydrous potassium carbonate and 50 ml ethyl-methyl ketone is heated under gentle reflux overnight. The reaction mixture is filtered to remove inorganic material and the filtrate evaporated down. The residue is purified by column chromatography on silica gel using hexane/ethyl acetate (1/1 v/v) as eluent and recrystallisation from acetonitrile to yield 1.2 g of 1,2,3,4-tetrakiskis(6-[4-{2-oxo-2H-1-benzopyran-7-yloxycarbonyl}phenoxy]hexanoyloxy)pentaerythritol.

The 2-oxo-2H-1-benzopyran-7-yl 4-hydroxybenzoate required as starting material was prepared as follows:

13.4 g triphenylphosphine is added to a solution of 8.3 g 7-hydroxycoumarin, 10.0 g 4-methoxycarbonyloxybenzoic acid, 8.9 g diethyl azodicarboxylate and 50 ml tetrahydrofuran at 0°C. The reaction mixture was stirred overnight at room temperature, filtered to remove inorganic material and the filtrate evaporated down, taken up in warm hexane, filtered to remove inorganic material and evaporated down again. The residue is purified by column chromatography on silica gel using hexane/ethyl acetate (1/1 v/v) as eluent and recrystallisation from acetonitrile to yield 12.2 g of 2-oxo-2H-1-benzopyran-7-yl 4-methoxycarbonyloxybenzoate.

50 ml of saturated ethanolic ammonia solution is added dropwise to a solution of 12.2 g of 2-oxo-2H-1-benzopyran-7-yl 4-methoxycarbonyloxybenzoate in 200 ml of ethanol. The reaction mixture is stirred for two hours, evaporated down and taken up in 100 ml diethyl ether. This solution is washed with water, dried , filtered to remove inorganic material and the filtrate evaporated down. The residue is purified by column chromatography on silica gel using hexane/ethyl acetate (1/1 v/v) as eluent and recrystallisation from acetonitrile to yield 9.5 g of 2-oxo-2H-1-benzopyran-7-yl 4-hydroxybenzoate.

The following compounds can be prepared in an analogous manner:

1,2,3,4-tetrakiskis(3-[4-{2-oxo-2H-1-benzopyran-7-yloxycarbonyl}phenoxy]propanoyloxy)pentaerythritol.
1,2,3,4-tetrakiskis(4-[4-{2-oxo-2H-1-benzopyran-7-yloxycarbonyl}phenoxy]butanoyloxy)pentaerythritol.
1,2,3,4-tetrakiskis(5-[4-{2-oxo-2H-1-benzopyran-7-yloxycarbonyl}phenoxy]pentanoyloxy)pentaerythritol.
1,2,3,4-tetrakiskis(7-[4-{2-oxo-2H-1-benzopyran-7-yloxycarbonyl}phenoxy]heptanoyloxy)pentaerythritol
1,2,3,4-tetrakiskis(8-[4-{2-oxo-2H-1-benzopyran-7-yloxycarbonyl}phenoxy]octanoyloxy)pentaerythritol
1,2,3,4-tetrakiskis(3-[4-{2-oxo-2H-1-benzopyran-6-yloxycarbonyl}phenoxy]propanoyloxy)pentaerythritol.

1,2,3,4-tetrakiskis(4-[4-{2-oxo-2H-1-benzopyran-6-yloxycarbonyl}phenoxy]butanoyloxy)pentaerythritol.

1,2,3,4-tetrakiskis(5-[4-{2-oxo-2H-1-benzopyran-6-yloxycarbonyl}phenoxy]pentanoyloxy)pentaerythritol.

1,2,3,4-tetrakiskis(6-[4-{2-oxo-2H-1-benzopyran-6-yloxycarbonyl}phenoxy]hexanoyloxy)pentaerythritol.

1,2,3,4-tetrakiskis(7-[4-{2-oxo-2H-1-benzopyran-6-yloxycarbonyl}phenoxy]heptanoyloxy)pentaerythritol

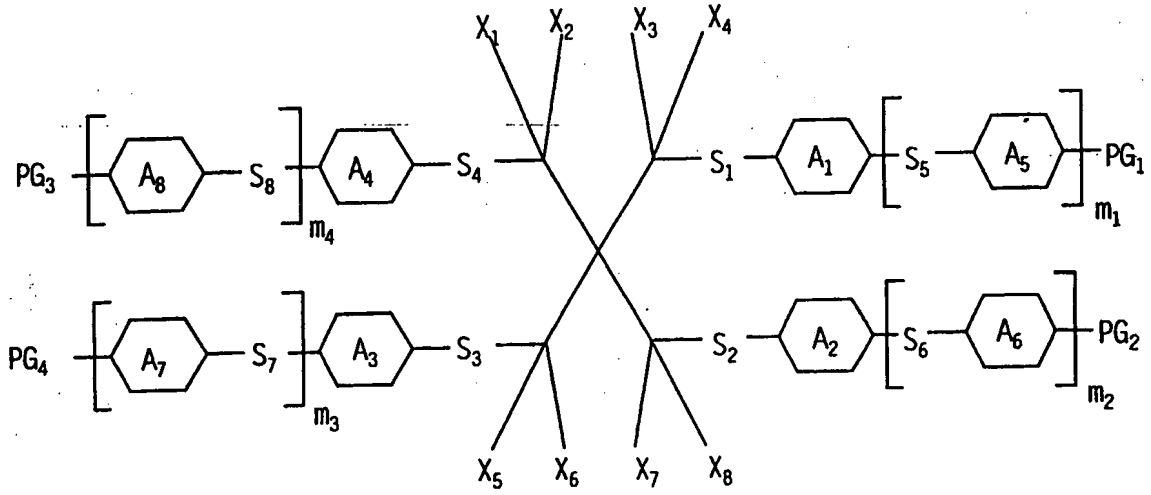
1,2,3,4-tetrakiskis(8-[4-{2-oxo-2H-1-benzopyran-6-yloxycarbonyl}phenoxy]octanoyloxy)pentaerythritol

Example 4. Preparation of Aligned Twisted and Planar Nematic Cells

A 2 w/w% solution of 1,2,3,4-tetrakis(8-[2-oxo-2H-1-benzopyran-7-yloxy]octanoyloxy)pentaerythritol in cyclopentanone was spin coated at 3000 rpm for 30 seconds onto indium tin oxide glass substrates (24 x 25 mm^2). The coated substrates were dried at 80°C for 30 min and then illuminated with linearly polarised ultra-violet light at 300.5 nm from an argon ion laser using the set-up shown in figure 4. The film anisotropy against UV exposure time was measured by determining the induced birefringence using a He-Ne laser at 632.8 nm. By the method described Twisted and non-twisted nematic cells were prepared by combining the photoaligned substrate with a unidirectionally rubbed polyimide substrate whose orientation direction was either parallel or orthogonal to that of the photoaligned substrate. An uniform cell gap was obtained by using mylar spacers (17 µm). The cells were filled with a nematic mixture (Merck E202) at 89°C under vacuum by capillary action. On cooling either a twisted nematic or a non-twisted cell was observed depending on how the substrates were combined. A twist angle of 90° was found for a twisted nematic cell using this cross-linked material exposed for 8 min at 2 $mWcm^{-2}$.

Claims

1. A compound of Formula I:



Formula I

wherein

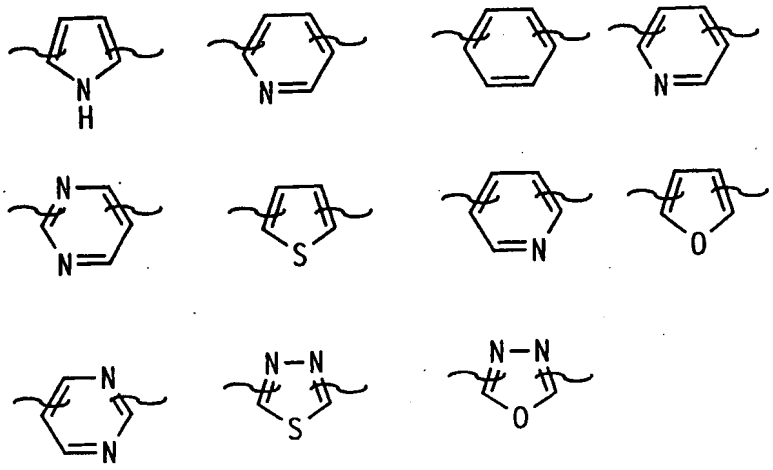
X_{1-8} are each independently selected from: H, halogen, CN, OH, straight or branched chain alkyl having from 1 to 16 carbon atoms, where one or more non-adjacent CH_2 groups may be substituted by CH(CN), $CH(CF_3)$, CHF, CHCl, $CH(CH_3)$;

S_{1-8} are spacer units;

PG_{1-4} are photopolymerisable/dimerisable groups;

m_1, m_2, m_3, and m_4 are each independently selected from the integers 1 and 0;

A_{1-8} are each independently selected from the aromatic rings:



where ⁓ indicates a sigma bond between part of the molecule shown in formula I and a carbon atom at any position in one of the aromatic rings;

and where the CH groups present in the aromatic rings may each be independently substituted by C(CN), $C(CF_3)$, C-halogen, $C(CH_3)$, CR, where R is selected from straight or branched chain alkyl and may include from 1 to 8 carbon atoms and including where one or more non-adjacent CH_2 groups may be substituted by CH(CN), $CH(CF_3)$, CHF, CHCl, $CH(CH_3)$.

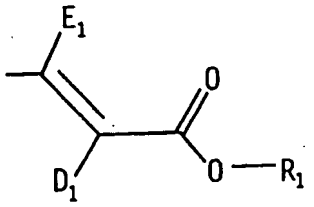
2. A compound according to Claim 1 wherein S_{1-4} are, independently of one another, selected from groups having the general formula:

$$L_1—(CH_2)_n—L_2$$

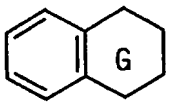
where: n = 1 to 30, where each CH_2 group present in the chain linking L_1 and L_2 may be independently substituted by CH(CN), $CH(CF_3)$, CHF, CHCl, $CH(CH_3)$, L_1 and L_2 are independently selected from: single covalent bond, O, COO, OOC, CH_2O, and OCH_2; and S_{5-8} are each independently selected from: COO, OOC, C≡C, C=C, single covalent bond.

3. A compound according to Claim 1 wherein S_{1-4} are independently selected from oxycarbonylalkanoyloxy, oxyalkoxy, oxycarbonylalkoxy, oxyalkanoyloxy, oxycarbonylphenoxyalkanoyloxy, oxyalkoxyalkyl containing from 1-16 carbon atoms.

4. A compound according to Claim 1 wherein PG_{1-4} are, independently of one another, selected from:



or



or

where a sigma bond exists between part of the molecule shown in Formula I and any one of the four C atoms that are in the benzene ring to which G is fused and that do not form part of the ring G, and where CH groups present in the benzene ring, to which the ring G is fused,

may each be independently substituted by C(CN), $C(CF_3)$, C-halogen, $C(CH_3)$, CR, where R is selected from straight or branched chain alkyl and may include from 1 to 8 carbon atoms and including where one or more non-adjacent CH_2 groups may be substituted by CH(CN), $CH(CF_3)$, CHF, CHCl, $CH(CH_3)$;

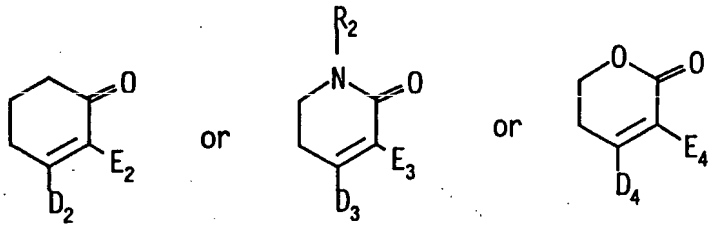
R_1 may be H, halogen, CN, NO_2, NCS, SCN, alkyl with 1 to 12 carbon atoms which is optionally substituted with one or more fluorines and in which optionally 1 or 2 non-adjacent methylene units (CH_2) can be replaced by oxygen, COO, OOC, CO and/or CH=CH;

D_1 may be H, alkyl or alkoxy with 1 to 8 carbon atoms, trifluoromethyl, or phenyl which may be substituted from one and up to and including all available substitution positions with one or more of the groups selected from CN, halogen, NO_2;

E_1 may be H, alkyl or alkoxy with 1 to 8 carbon atoms, cyano, or $COOR_5$;

R_5 may be C_{1-10} alkyl;

where G is independently selected from:



or

or

R_2 may be H or C_{1-10} alkyl;

D_2 may be H, alkyl or alkoxy with 1 to 8 carbon atoms, trifluoromethyl, or phenyl which may be substituted from one and up to and including all available substitution positions with one or more of the groups selected from CN, halogen, NO_2;

E_2 may be H, alkyl or alkoxy with 1 to 8 carbon atoms, cyano, or $COOR_6$;

R_6 may be C_{1-10} alkyl.

D_3 may be H, alkyl or alkoxy with 1 to 8 carbon atoms, trifluoromethyl, or phenyl which may be substituted from one and up to and including all available substitution positions with one or more of the groups selected from CN, halogen, NO_2;

E_3 may be H, alkyl or alkoxy with 1 to 8 carbon atoms, cyano, or $COOR_7$;

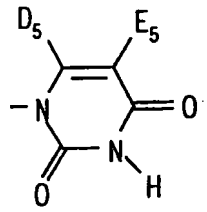
R_7 may be C_{1-10} alkyl.

D_4 may be H, alkyl or alkoxy with 1 to 8 carbon atoms, trifluoromethyl, or phenyl which may be substituted from one and up to and including all available substitution positions with one or more of the groups selected from CN, halogen, NO_2;

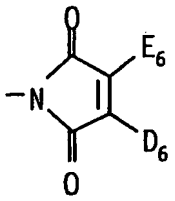
E_4 may be H, alkyl or alkoxy with 1 to 8 carbon atoms, cyano, or $COOR_8$;

R_8 may be C_{1-10} alkyl.

and where J is independently selected from:



or



D_5 may be H, alkyl or alkoxy with 1 to 8 carbon atoms, trifluoromethyl, or phenyl which may be substituted from one and up to and including all available substitution positions with one or more of the groups selected from CN, halogen, NO_2;

E_5 may be H, alkyl or alkoxy with 1 to 8 carbon atoms, cyano, or $COOR_9$;

R_9 may be C_{1-10} alkyl.

D_6 may be H, alkyl or alkoxy with 1 to 8 carbon atoms, trifluoromethyl, or phenyl which may be substituted from one and up to and including all available substitution positions with one or more of the groups selected from CN, halogen, NO_2;

E_6 may be H, alkyl or alkoxy with 1 to 8 carbon atoms, cyano, or $COOR_{10}$;

R_{10} may be C_{1-10} alkyl.

5. An alignment layer suitable for use in a liquid crystal device comprising a compound according to any of claims 1-4.

6. A method of providing an alignment layer on a surface of a liquid crystal cell wall comprising the steps of
depositing a layer of material comprising at least one compound according to any of claims 1-4 on the surface;
exposing the material to actinic radiation.

7. A method according to Claim 6 characterised in that the method further comprises the step of controlling the exposure time and/or intensity of the actinic radiation used to provide a selected value of pretilt in a liquid crystal placed in contact with the exposed layer.

8. A liquid crystal device comprising a layer of liquid crystal material between two cell walls, the cell walls at least one carrying electrode structures and surface treated to provide an alignment layer for liquid crystal molecules;
characterised in that the alignment layer comprises a compound according to any of claims 1-4 which has been exposed to actinic radiation.

9. A liquid crystal device according to Claim 8 characterised in the alignment layer comprises a compound according to Claims 1-4 that has been exposed to actinic radiation, the exposure time and/or intensity of the actinic radiation used being controlled to provide a selected value of pretilt in a liquid crystal placed in contact with the exposed layer.

11. A liquid crystal device according to claim 7 wherein the device is an Active Matrix Device.

12. A liquid crystal device according to either of claims 7 and 8 wherein the device is an STN device.

13. A method according to claim 6 wherein the radiation is in the range 250-450nm.

14. A device according to claim 7 wherein the radiation is in the range 250-450nm.

Fig.1.

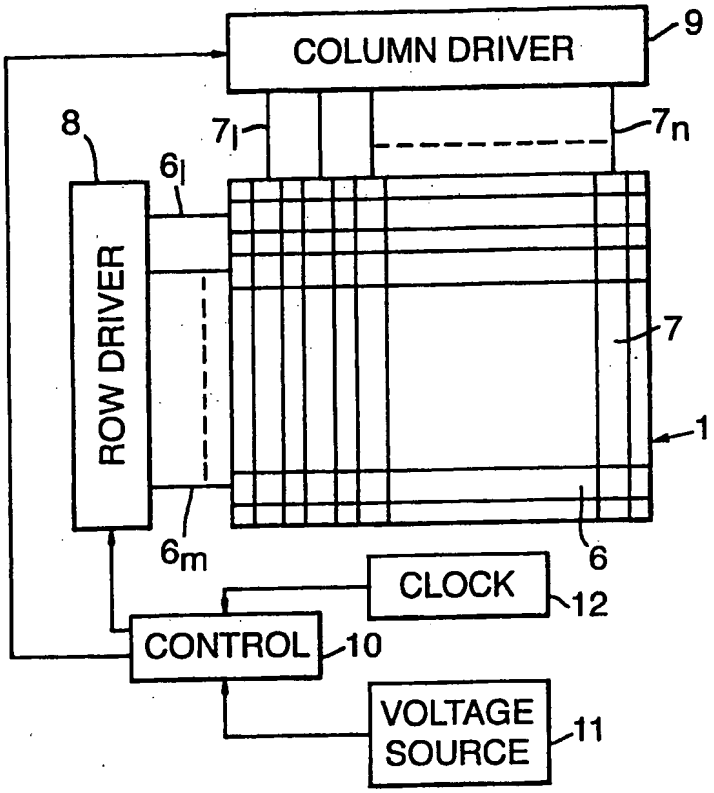


Fig.2.

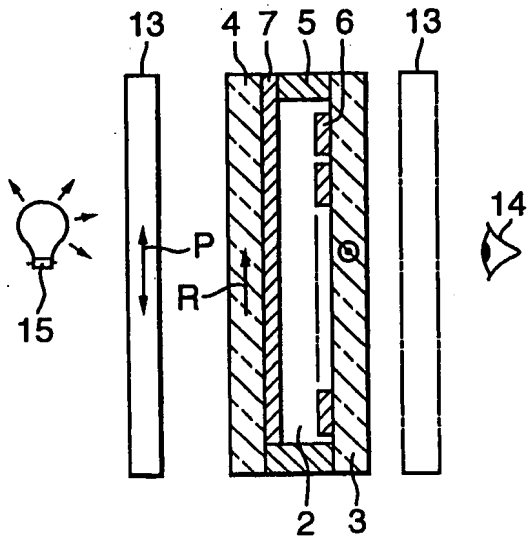


Fig.3.

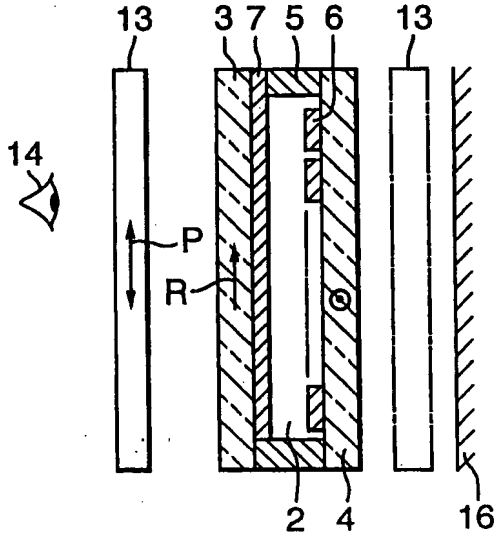
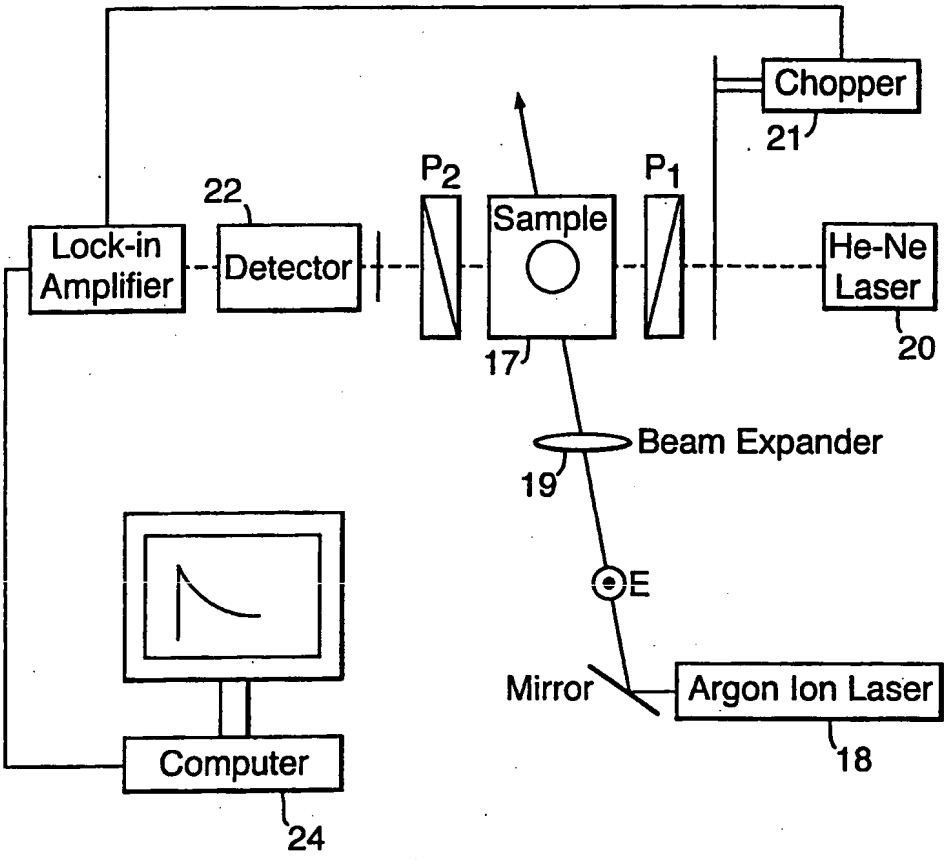


Fig.4.


Chopper
21
22
P2
P1
Sample
Lock-in Amplifier
Detector
He-Ne Laser
20
17
Beam Expander
19
E
Mirror
Argon Ion Laser
18
Computer
24

INTERNATIONAL SEARCH REPORT

Inter xnal Application No
PCT/GB 00/00825

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07D311/16 C07C69/618 G02F1/1337

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07D C07C G02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DANUSSO, F. ET AL: "Structure and solid state photopolymerization of pentaerythrito tetracinnamate" , POLYMER (1977), 18(2), 161-3 XP000910961 the whole document	1,2,4
P,A	VAN DE WITTE, PETER ET AL: "Optical components from a new vitrifying liquid crystal" , LIQ. CRYST. (1999), 26(7), 1039-1046 XP000911037 the whole document	1
A	WO 96 10049 A (HOFFMANN LA ROCHE ;HERR ROLF PETER (DE); HERZOG FRANCOIS (FR); SCH) 4 April 1996 (1996-04-04) the whole document	1,5,6, 8-12

-/—

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 May 2000	19. 06. 00

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Puetz, C

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Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Inter xnal Application No
PCT/GB 00/00825

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 611 786 A (HOFFMANN LA ROCHE) 24 August 1994 (1994-08-24) cited in the application the whole document	1,5,6, 8-12

3

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

I. .national application No.
PCT/GB 00/00825

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 1-14 (all partially)
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-14 (all partially)

Present claims 1-14 relate to an extremely large number of possible compounds, as well as alignment layers comprising the claimed compounds, method for providing such alignment layers and liquid crystal devices comprising such alignment layers. Support within the meaning of PCT Article 6 and / or disclosure within the meaning of PCT Article 5 is to be found, however, for only a very small proportion of the compounds, alignment layers, methods and liquid crystal devices claimed. In the present case, the
claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the compounds recited in the examples and a reasonable generalisation thereof. Compounds of example 1, page 13, line 15 to page 14, line 18 as well as example 4 are not considered to fall within the scope of the claims (the requirements of PCT Article 6 are not considered met) and thus have not been searched.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 00/00825

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		DE 59507348 D	05-01-2000
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		JP 6287453 A	11-10-1994
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